

PATENT ABSTRACTS OF JAPAN

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(54) FLAME-RETARDANT SHEET AND THERMOFORMED ARTICLE

(57)Abstract:

PURPOSE: To provide a formed article produced by the deep draw forming of a polybutylene terephthalate sheet having excellent flame-retardancy and thermoformability.

CONSTITUTION: The objective sheet is produced by compounding (A) 60-90 pts.wt. of polybutylene terephthalate with (B) 1-20 pts.wt. of a polyarylate and/or polyester elastomer, (C) 5-25 pts.wt. of a flame-retardant consisting of a bromine compound, (D) 0-15 pts.wt. of a flame-retarding assistant consisting of an antimony compound and (E) ≤ 2 wt.% (based on the sum of A to D) of fine powder of polytetrafluoroethylene. A thermoformed article is produced by forming the sheet under heating.

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1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

[Claim(s)]

[Claim 1] (A) The fire-resistant sheet which consists of a constituent which blended 0 - 2 % of the weight of (E) fines-like polytetrafluoroethylenes to the total quantity of polyethylene terephthalate 60 - 90 weight sections, (B) polyarylate or/and the polyester elastomer 1 - 20 weight sections, the flame retarder 5 which consists of a (C) bromine compound - 25 weight sections, the fire-resistant assistant 0 which consists of a (D) antimony compound - 15 weight sections and said component (A) thru/or (D).

[Claim 2] The thermoforming article which comes to fabricate the fire-resistant sheet of claim 1 under heating.

[Detailed Description of the Invention]

[0001]

[Industrial Application] It is related with the mold goods which use this sheet for the sheet list which was excellent in the fire retardancy which made polybutylene terephthalate the subject, and was excellent in thermoforming nature, and come to carry out thermoforming.

[0002]

[Problem(s) to be Solved by the Invention] Generally the sheet which consists of polybutylene terephthalate is difficult thermoforming. Moreover, polybutylene terephthalate tends to burn, especially when it is made into a thin sheet.

[0003] This invention means also endowing fire retardancy with coincidence while endowing thermoforming nature with such polybutylene terephthalate.

[0004] Therefore, this invention relates to development of the new material which carries out deep drawing of the sheet of polybutylene terephthalate.

[0005]

[Elements of the Invention] This invention sheet-izes the resin constituent which kneaded 0 - 1 % of the weight (PHR) of (E) fines-like fluororesin to the total quantity of (A) polyethylene terephthalate 60 - 90 weight sections, (B) polyarylate or/and the polyester elastomer 1 - 20 weight sections, (C) bromination polystyrene 5 - 25 weight sections, the (D) antimony compound 0 - 15 weight sections and (A), (B), (C), and (D). Moreover, the thermoforming article excellent in fire retardancy is obtained by carrying out thermoforming of such a sheet.

[0006] Hereafter, this invention is explained in full detail.

[0007] although it is polyester which (A) polybutylene terephthalate used for this invention uses a terephthalic acid as an acid component, and uses a butylene glycol as a glycol component -- glycol components other than dicarboxylic acid other than a terephthalic acid and/or hydroxy acid, or a butylene glycol -- small quantity, for example, less than [10 mol %], -- desirable -- about [5 mol % less than] -- even if contained, it does not interfere.

[0008] Aromatic series dicarboxylic acid other than a terephthalic acid, for example, a phthalic acid, isophthalic acid, naphthalene dicarboxylic acid, diphenyl dicarboxylic acid, diphenyl ether dicarboxylic acid, difenoxycarboxylic acid, diphenylmethane dicarboxylic acid, diphenyl ketone dicarboxylic acid, diphenyl sulfide dicarboxylic acid, diphenyl sulfone dicarboxylic acid, aliphatic series dicarboxylic acid, for example, a succinic acid, an adipic acid, a sebacic acid, alicycle group dicarboxylic acid, for example, cyclohexane dicarboxylic acid, tetralin dicarboxylic acid, decalin dicarboxylic acid, etc. are illustrated.

[0009] As a glycol component, they are ethylene glycol and propylene glycol, A trimethylene glycol, pentamethylene glycol, hexamethylene glycol, an octamethylene glycol, neopentyl glycol, cyclohexane dimethanol, a xylylene glycol, a diethylene glycol, a polyethylene glycol, bisphenol A, a catechol, resorcinol, hydroquinone, dihydroxydiphenyl, dihydroxy diphenyl ether, dihydroxy diphenylmethane, dihydroxy diphenyl ketone, a dihydroxydiphenyl sulfide, dihydroxydiphenyl sulfone, etc. are illustrated.

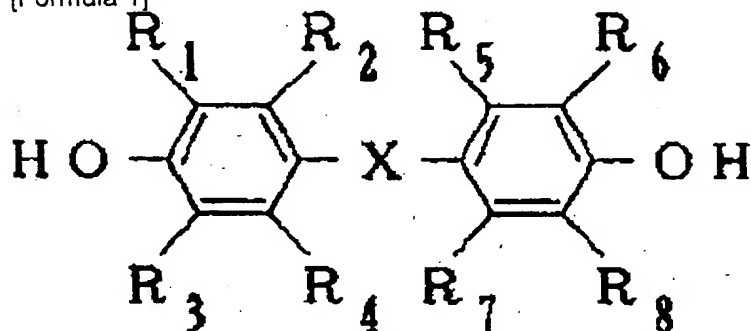
[0010] As a hydroxy acid component, an oxy-benzoic acid, a hydroxy naphthoic acid, a

hydroxy diphenyl carboxylic acid, an omega-hydroxy caproic acid, etc. are illustrated.
 [0011] Moreover, polyester may copolymerize the compound of three or more organic functions, for example, a glycerol, a trimethyl propane, pentaerythritol, trimellitic acid, pyromellitic acid, etc. in the range which does not lose moldability ability substantially.
 [0012] This polyester carries out the polycondensation of a terephthalic acid and/or its functional derivative, a butylene glycol, and/or its functional derivative using a well-known aromatic polyester manufacturing method conventionally, and is obtained. Moreover, little direction is desirable although there is especially no limit in the end carboxyl group concentration of PBT used in this invention.

[0013] The polyarylate resin of the (B) component used by this invention is the following general formula (** 1).

[0014]

[Formula 1]



[0015] It comes out, and is obtained from the bisphenol compound and aromatic series dicarboxylic acid which are expressed, -X- is either -O-, -S-, -SO₂-, -CO- and an alkylene group here, and it is R₁-R₈. They are hydrogen, the alkyl group of carbon numbers 1-8, or a halogen.

[0016] As the bisphenol compound of the above-mentioned general formula (** 1), For example, 4 and 4'-dihydroxy-diphenyl ether, the screw (4-hydroxy-2-methylphenyl) ether, The screw (4-hydroxy-3-chlorophenyl) ether, screw (4-hydroxyphenyl) sulfide, A screw (4-hydroxyphenyl) ketone, screw (4-hydroxyphenyl) methane, Screw (4-hydroxy-3-methylphenyl) methane, screw (4-hydroxy - 3, 5-dichlorophenyl) methane, Screw (4-hydroxy - 3, 5-dibromo phenyl) methane, 1, and 1-screw (4-hydroxyphenyl) ethane, 2 and 2-screw (4-hydroxyphenyl) propane, 2, and 2-screw (4-hydroxy-3-methylphenyl) propane, 2 and 2-screw (4-hydroxy-3-chlorophenyl) propane, 2, and 2-screw (4-hydroxy - 3, 5-dichlorophenyl) propane, 2 and 2-screw (4-hydroxy - 3, 5-dibromo phenyl) propane, 1 and 1-screw (4-hydroxyphenyl) butane, a screw (4-hydroxyphenyl) phenylmethane, Screw (4-hydroxyphenyl) diphenylmethane, screw (4-hydroxyphenyl)-4'-methylphenyl methane, 1 and 1-screw (4-hydroxyphenyl) - 2, 2, and 2-trichloroethane, Screw (4-hydroxyphenyl)-(4'-chlorophenyl) methane, 1 and 1-screw (4-hydroxyphenyl) cyclohexane, 1, 4-screw (4-hydroxyphenyl) cyclohexane, 2, and 2-screw (4-hydroxy naphthyl) propane etc. is raised, and 2 and 2-screw (4-hydroxyphenyl) propane is especially desirable. Moreover, two or more sorts of mixture is sufficient as these bisphenol compounds, and they may use mixture with other divalent compound, 2 [for example,], and 2'-dihydroxydiphenyl, dihydroxy naphthalene, hydroquinone, resorcinol, 2, 6-dihydroxy chlorobenzene, 2, 6-dihydroxy toluene, 3, and 6-dihydroxy toluene etc. further.

[0017] As aromatic series dicarboxylic acid, a terephthalic acid, isophthalic acid, or such mixture are desirable. Moreover, these terephthalic acids and isophthalic acid may be permuted by the halogen or the alkyl group of carbon numbers 1-8. Furthermore, in addition to these, other little aromatic series or aliphatic series dicarboxylic acid, or its functional derivative may be copolymerized.

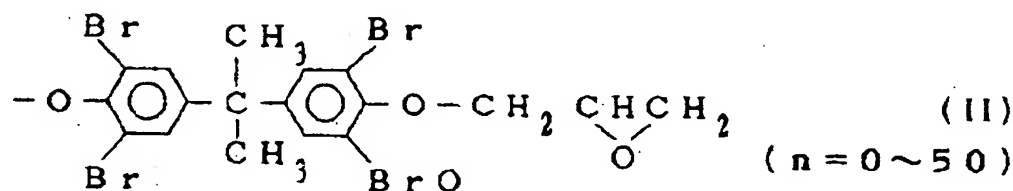
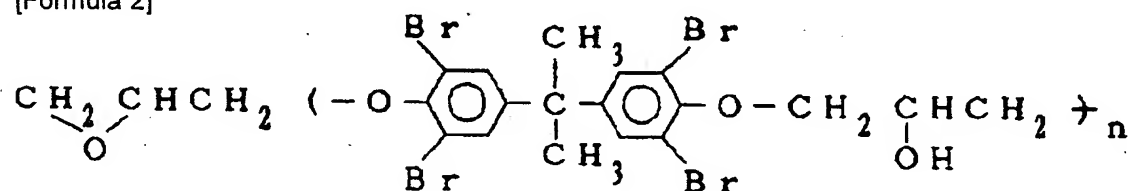
[0018] Although the polyester elastomer used for this invention generally consists of an aromatic series dicarboxylic acid component (1), a with a carbon numbers of three or more low-molecular-weight glycol component (2), and a polyoxy-alkylene-glycol component (3), it is desirable that more than 70mol% consists of heat-resistant fields of one sort of

[0019] As the aforementioned (1) component, although terephthalic-acid, isophthalic acid, 2, 6-naphthalene dicarboxylic acid, 2, 7-naphthalene dicarboxylic acid, 1, 5-naphthalene dicarboxylic acid, 4, and 4'-diphenyl ether dicarboxylic acid, 4, and 4'-diphenylsulfone dicarboxylic acid, 4, and 4'-difenoxycarboxylic acid etc. can be considered, terephthalic-acid and 2, and 6-naphthalene dicarboxylic acid is mentioned especially preferably. This dicarboxylic acid may use two or more sorts together, using only one sort.

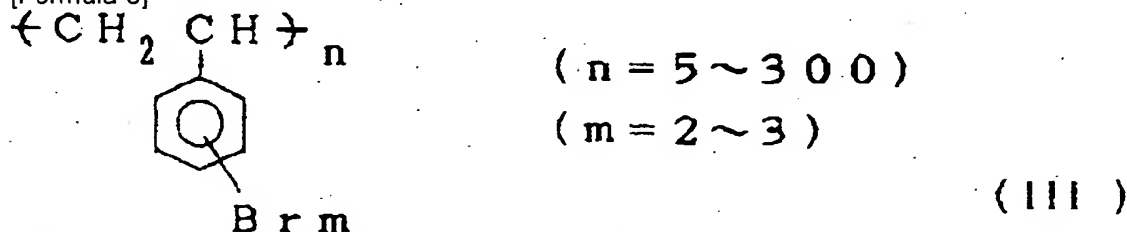
[0021] As the aforementioned (3) component, a polyoxypropylene glycol, Polly 1, 2-butylene ether glycol, polyoxy tetramethylene glycol, a polyoxypentamethylene glycol, polyoxy hexamethylene glycol, polyoxyheptamethylene glycol, a polyoxy octamethylene glycol, polyoxynonamethylene glycol, etc. can be considered. It is polyoxy tetramethylene glycol especially preferably in these. Of course, that to which copolymerization of these polyoxy alkylene glycol was carried out can also use random and the thing by which block copolymerization was carried out.

[0023] A bromination bisphenol A mold polycarbonate, bromination epoxy, bromination polystyrene, bromination imide, bromination diphenyl ether, etc. are mentioned to the flame retarder (C) which consists of a bromine compound used for this invention.

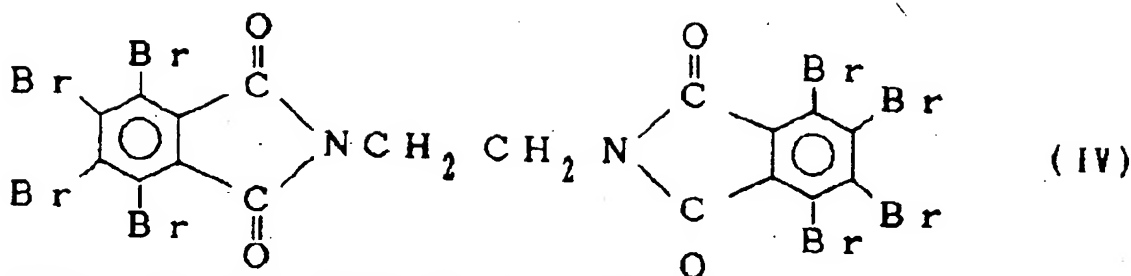
[Formula 2]



[Formula 3]

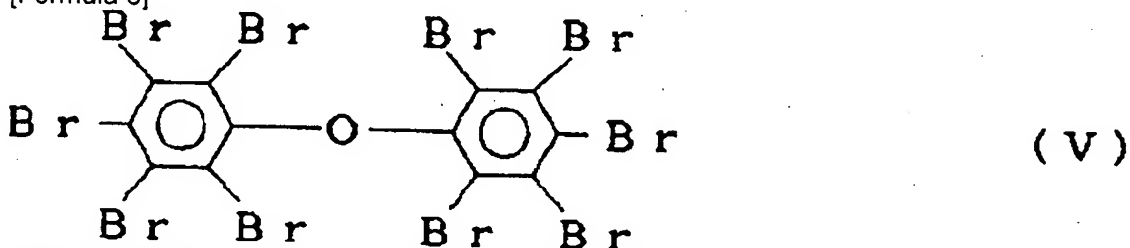


[Formula 4]



[0027] The bromination diphenyl ether flame retarder used for this invention is the following chemical formula (V).

[Formula 5]



[0028] The addition of the flame retarder used by this invention is 5 - 25 weight section. so that there are many additions of the inorganic bulking agent in [all] a constituent -- moreover, Sb 2O3 etc. -- although the addition of a flame retarder can be lessened when a fire-resistant assistant is used together, the at least 5 weight section is required, and, in the case of not more than it, the fire retardancy of the constituent obtained is still inadequate. Conversely, since distribution of a flame retarder is bad when [than 25 weight sections] more, extrusion nature and a moldability fall, and the reinforcement of the mold goods obtained does not become low and have them, either. [desirable]

[0029] In addition, although only one sort may be used, a flame retarder is not cared about even if two or more sorts are used together. However, the total quantity of the used flame retarder must be within the limits of 5 - 25 weight section.

[0030] Next, Sb 2O3 used by this invention And/or, as for the fire-resistant assistant (D) shown by $x\text{Na}_2\text{O} \cdot y\text{Sb}_2\text{O}_5$ and $y\text{H}_2\text{O}$ ($x=0-1$, $y=0-4$), it is desirable to blend in order to raise fire-resistant effectiveness. Although particle size is not limited, 0.02-5 micrometers is desirable.

[0031] Moreover, surface treatment may be carried out if needed by an epoxy compound, the silane compound, the isocyanate compound, the silane compound, the titanate compound, etc. Although it is 0 - 15 weight section, since the addition of a fire-resistant assistant needs to add many flame retarders when not adding a fire-resistant assistant, it is good to add the fire-resistant assistant of 20 - 70 weight section to a flame retarder preferably. Moreover, it falls [disassembly of resin or a compounding agent may be promoted and / the reinforcement of mold goods] and is not desirable when there are more additions than 15 weight sections.

[0032] Next, the (E) fines-like polytetrafluoroethylene used for this invention was manufactured according to the emulsion polymerization, and the particle size has desirable 0.05-0.5 micrometers at a primary particle.

[0033] Unless fire-resistant effectiveness is spoiled to this (E), it is also possible to carry out little copolymerization of the monomers, such as perfluoroalkyl vinyl ether. An addition is 0-2PHR. (E) It is hard coming to drop a melting polymer at the time of fire retardancy, it **** at it, and it is hard coming to generate the secondary combustion by dropping by adding a component.

[0034] Since a desired property is further given to the polyester resin constituent of this invention according to the purpose, other additives, for example, an inorganic bulking agent, a coloring agent, an ultraviolet ray absorbent, a release agent, an antistatic agent, etc. can be added in the range which does not spoil the physical properties remarkably.

[0035] Next, how to sheet-ize the constituent which constitutes the sheet of this invention is described. The sheet of this invention is obtained by supplying the constituent or/and

component which constitute this invention, extruding through a slit-like dice, cooling, making the well-known facility generally used and an approach, i.e., an extruder, solidify in casting drum lifting, and sheet-izing.

[0036] As the approach of supplying the constituent and/or component of this invention to an extruder, for example, the approach of carrying out melting kneading extrusion with an extruder, adjusting a pellet, and creating a sheet using this pellet after an appropriate time, after mixing ** each component and ** -- the pellet with which presentations once differ can adjust and any approaches, such as the approach of carrying out specified-quantity mixing of the pellet, supplying the extruder of sheet creation, and obtaining a sheet, and the approach of teaching 1 of each component or 2 or more directly to the extruder of ** sheet creation, can use. Moreover, in addition to this, a creation sheet, a thermoforming article, and/or when thermoforming is carried out, it keeps generating and what ground and flake-ized waste can also once be used as 1 of the ingredient in the case of sheet-izing of ** - **, or a component. Moreover, it is desirable to mix components other than this and to add a part of component as fine fine particles, when performing homogeneity combination of these components. In addition, it is desirable to precede to supply a pellet and a component to an extruder and to dry.

[0037] As an approach of drying a pellet, the approach of dehumidifying air or nitrogen gas heated above 100 degrees C to the temperature the temperature of temperature lower 30 degrees C than the melting point of polyester within the limits and within the limits of the temperature more desirable and lower 50 degrees C than the melting point of polyester above 120 degrees C if needed, using it, and drying, the approach of drying using an electromagnetic wave, etc. are applied, for example.

[0038] Moreover, if the load of static electricity is carried out to a film or a sheet and it is made to make it stick to a cooling drum in the case of casting, the film or sheet which was excellent in smoothness can be obtained.

[0039] Although thermoforming may not be given but decision etc. may use as it is by carrying out the sheet of this invention which were obtained by carrying out like ****, it can use for still more various applications by carrying out thermoforming of this sheet.

[0040] Thermoforming is presented with it after the preheating of the film or sheet which were obtained by carrying out like the above is carried out by an infrared heater, a hot-platen heater, or hot blast.

[0041] A vacuum forming, pressure forming, or vacuum pressure sky shaping is adopted using a female or a female, a male, or a plug as the approach of thermoforming. A female, a male, and a plug can be heated on the occasion of shaping.

[0042]

[Application] Although the thermoforming article it is unrefined from the fire-resistant sheet obtained by this invention and this sheet is beneficially used for insulating materials, such as machine parts, such as components of the electrical and electric equipment and electronic equipment, components of OA equipment, and a power tool, or a motor, the base material of a card, a building material, etc., especially that application is not limited.

[0043]

[Working Example(s) and Comparative Example(s)] Hereafter, this invention is explained in full detail by the example and the example of a comparison. It evaluated by carrying out the fire retardancy of a **** sheet, and a moldability as following to this invention.

[0044] Flammability: According to the approach of the subject 94 (UL-94) of Underwriters Laboratories, flammability was examined using five test pieces and the combustion grade was evaluated based on UL-94.

[0045] Thermoforming nature: Tray-like metal mold was equipped with and fabricated to an Asano lab FC-1 APA-W mold vacuum pressure sky making machine, and it evaluated by observing a shaping condition.

[0046] the resin which carried out melting kneading by the presentation indicated to Table 1 -
- ***** -- the pellet was created, further, after drying at 130 degrees C for 5 hours, melting extrusion of this pellet was carried out, and it was sheet-ized. Sheet thickness was 0.3mm.

[0047] Subsequently, about this sheet, the flammability and thermoforming nature were evaluated and the result was summarized in Table 2.

[0048] In addition, each component used for this example and the example of a comparison is as follows.

(A) Polyethylene terephthalate (PET)

(B) Polyarylate (PAr)

Polyester elastomer (Ela)

(C) Bromination polystyrene (Br-izing PSt)

Bromination bisphenol A mold polycarbonate (Br-ized PC)

Bromination epoxy (Br-izing Epx)

(D) Antimony trioxide (Sb-O)

Sodium antimonate (Sb-Na)

(E) Fines-like polytetrafluoroethylene (PPTFE)

[0049]

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(B) Polyarylate (PAr)

Polyester elastomer (Ela)

(C) Bromination polystyrene (Br-izing PSt)

Bromination bisphenol A mold polycarbonate (Br-ized PC)

Bromination epoxy (Br-izing Epx)
(D) Antimony trioxide (Sb-O)
Sodium antimonate (Sb-Na)
(E) Fines-like polytetrafluoroethylene (PPTFE)
[0049]
[Table 1]

	組 成					特 性	
	(A)	(B)	(C)	(D)	(E)	熱成形性	燃焼性
実施例	1 PET: 82	PA: 7	Br化PSt: 8	Sb・O : 3	-	良	V-2
	2 PET: 68	Ela: 9	Br化PC :17	Sb・O : 7	-	良	V-0
	3 PET: 59	PA: 5 Ela: 6	Br化PC :22	Sb・Na: 8	-	良	V-0
	4 PET: 79	Ela: 8	Br化Epx:13	-	-	良	V-2
	5 PET: 91	PA: 6	Br化Epx:10	Sb・O : 3	P-PTFE:0.07	良	V-2
比較例	1 PET:100	-	-	-	-	良	HB
	2 PET: 90	PA: 7	Br化PSt: 8	Sb・O : 1	-	良	HB
	3 PET: 47	Ela:10	Br化PC :28	Sb・O :15	P-PTFE:2.5	不良	V-0

欄右側の数字は(A), (B), (C), (D):重量部、(E):PHRである。

(19) 日本国特許庁 (J P)

(12) 公開特許公報 (A)

(11) 特許出願公開番号

特開平6-65487

(43) 公開日 平成6年(1994)3月8日

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C 0 8 L 67/02	L P D	8933-4 J		
B 2 9 C 51/00		7421-4 F		
C 0 8 J 5/18	C F D	9267-4 F		
C 0 8 K 3/22	K J R	7242-4 J		
5/00	K J T	7242-4 J		

審査請求 未請求 請求項の数 2 (全 6 頁) 最終頁に続く

(21) 出願番号	特願平4-219246	(71) 出願人	000003001 帝人株式会社 大阪府大阪市中央区南本町1丁目6番7号
(22) 出願日	平成4年(1992)8月18日	(72) 発明者	正坊地 義行 神奈川県相模原市小山3丁目37番19号 帝人株式会社相模原研究センター内
		(72) 発明者	下間 昌 神奈川県相模原市小山3丁目37番19号 帝人株式会社相模原研究センター内
		(74) 代理人	弁理士 前田 純博

(54) 【発明の名称】 難燃シート及び熱成形品

(57) 【要約】

【目的】 難燃性と熱成形性に優れたポリブチレンテレフタレートシートを深絞り成形して得られる成形品の開発。

【構成】 (A) ポリブチレンテレフタレート60～90重量部、(B) ポリアリレート及び又はポリエステルエラストマー1～20重量部、(C) 臭素化合物よりなる難燃剤5～25重量部、(D) アンチモン化合物よりなる難燃助剤0～15重量部及び、上記(A)～(D)の合計量に対し、(E) 微粉状ポリテトラフルオロエチレン2重量%以下を配合した組成のシート並びに該シートを加熱下で成形してなる熱成形品。

【特許請求の範囲】

【請求項1】 (A) ポリエチレンテレフタレート60～90重量部、(B) ポリアリレート又は／及びポリエステルエラストマー1～20重量部、(C) 臭素化合物よりなる難燃剤5～25重量部、(D) アンチモン化合物よりなる難燃助剤0～15重量部及び、前記成分(A)乃至(D)の合計量に対し、(E) 微粉状ポリテトラフルオロエチレン0～2重量%を配合した組成物よりなる難燃シート。

【請求項2】 請求項1の難燃シートを加熱下で成形してなる熱成形品。

【発明の詳細な説明】

【0001】

【産業上の利用分野】 ポリブチレンテレフタレートを主体とした難燃性に優れ、かつ熱成形性に優れたシート並びにこのシートを用いて熱成形してなる成形品に関する。

【0002】

【発明が解決しようとする問題】 ポリブチレンテレフタレートよりなるシートは一般に熱成形が困難である。またポリブチレンテレフタレートは、特に薄いシートにした場合は燃焼しやすい。

【0003】 本発明は、このようなポリブチレンテレフタレートに熱成形性を賦与するとともに難燃性をも同時に賦与することを意図したものである。

【0004】 従って、本発明はポリブチレンテレフタレートのシートを深絞り加工する新しい素材の開発に係わるものである。

【0005】

【発明の構成】 本発明は、(A) ポリエチレンテレフタレート60～90重量部、(B) ポリアリレート又は／及びポリエステルエラストマー1～20重量部、(C) 臭素化ポリスチレン5～25重量部、(D) アンチモン化合物0～15重量部及び、(A)、(B)、(C)及び(D)の合計量に対し、(E) 微粉状弗素樹脂0～1重量%(PHR)を混練した樹脂組成物をシート化したものである。また、このようなシートを熱成形することによって難燃性に優れた熱成形品を得るものである。

【0006】 以下、本発明を詳述する。

【0007】 本発明に用いる(A) ポリブチレンテレフタレートは、テレフタル酸を酸成分とし、ブチレングリコールをグリコール成分とするポリエステルであるが、テレフタル酸以外のジカルボン酸及び／又はオキシカルボン酸やブチレングリコール以外のグリコール成分が少量、例えば10モル%以下、好ましくは5モル%以下程度含まれていても差支えない。

【0008】 テレフタル酸以外の芳香族ジカルボン酸、例えばフタル酸、イソフタル酸、ナフタレンジカルボン酸、ジフェニルジカルボン酸、ジフェニルエーテルジカルボン酸、ジフェノキシエタンジカルボン酸、ジフェニ

ルメタンジカルボン酸、ジフェニルケトンジカルボン酸、ジフェニルスルフィドジカルボン酸、ジフェニルスルホンジカルボン酸、脂肪族ジカルボン酸、例えばコハク酸、アジピン酸、セバシン酸、脂環族ジカルボン酸、例えばシクロヘキサレンジカルボン酸、テトラリンジカルボン酸、デカリンジカルボン酸等が例示される。

【0009】 グリコール成分としてはエチレングリコール、プロピレングリコール、トリメチレングリコール、ペンタメチレングリコール、ヘキサメチレングリコール、オクタメチレングリコール、ネオペンチルグリコール、シクロヘキサンジメタノール、キシリレングリコール、ジエチレングリコール、ポリエチレングリコール、ビスフェノールA、カテコール、レゾルシノール、ヒドロキノン、ジヒドロキシジフェニル、ジヒドロキシジフェニルエーテル、ジヒドロキシジフェニルメタン、ジヒドロキシジフェニルケトン、ジヒドロキシジフェニルスルフィド、ジヒドロキシジフェニルスルホン等が例示される。

【0010】 オキシカルボン酸成分としては、オキシ安息香酸、ヒドロキシナフトエ酸、ヒドロキシジフェニルカルボン酸、ω-ヒドロキシカプロン酸等が例示される。

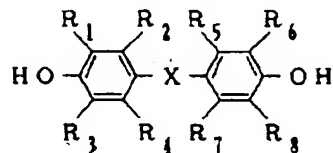
【0011】 また、ポリエステルが実質的に成形性能を失わない範囲で3官能以上の化合物、例えばグリセリン、トリメチルプロパン、ペンタエリスリトール、トリメリット酸、ピロメリット酸等を共重合してよい。

【0012】 かかるポリエステルは、テレフタル酸及び／又はその機能的誘導体とブチレングリコール及び／又はその機能的誘導体とを、従来公知の芳香族ポリエステル製造法を用いて重縮合させて得られる。また本発明において用いるPBTの末端カルボキシル基濃度には特に制限はないが、少ない方が望ましい。

【0013】 本発明で用いられる(B)成分のポリアリレート樹脂とは、下記一般式(化1)

【0014】

【化1】



【0015】 で表わされるビスフェノール化合物と芳香族ジカルボン酸とから得られるものであり、ここで-Xは、-O-、-S-、-SO₂-、-CO-及びアルキレン基のいずれかでありR₁～R₈は水素、炭素数1～8のアルキル基、ハロゲンのいずれかである。

【0016】 上記一般式(化1)のビスフェノール化合物としては、例えば4,4'-ジヒドロキシジフェニルエーテル、ビス(4-ヒドロキシ-2-メチルフェニ

ル) エーテル、ビス(4-ヒドロキシ-3-クロロフェニル) エーテル、ビス(4-ヒドロキシフェニル) サルファイド、ビス(4-ヒドロキシフェニル) ケトン、ビス(4-ヒドロキシフェニル) メタン、ビス(4-ヒドロキシ-3-メチルフェニル) メタン、ビス(4-ヒドロキシ-3, 5-ジクロロフェニル) メタン、ビス(4-ヒドロキシ-3, 5-ジブromoフェニル) メタン、1, 1-ビス(4-ヒドロキシフェニル) エタン、2, 2-ビス(4-ヒドロキシフェニル) プロパン、2, 2-ビス(4-ヒドロキシ-3-メチルフェニル) プロパン、2, 2-ビス(4-ヒドロキシ-3-クロロフェニル) プロパン、2, 2-ビス(4-ヒドロキシ-3, 5-ジクロロフェニル) プロパン、2, 2-ビス(4-ヒドロキシ-3, 5-ジブromoフェニル) プロパン、1, 1-ビス(4-ヒドロキシフェニル) ブタン、ビス(4-ヒドロキシフェニル) フェニルメタン、ビス(4-ヒドロキシフェニル) ジフェニルメタン、ビス(4-ヒドロキシフェニル) -4'-メチルフェニルメタン、1, 1-ビス(4-ヒドロキシフェニル) -2, 2, 2-トリクロロエタン、ビス(4-ヒドロキシフェニル) -4'-クロロフェニル) メタン、1, 1-ビス(4-ヒドロキシフェニル) シクロヘキサン、1, 4-ビス(4-ヒドロキシフェニル) シクロヘキサン、2, 2-ビス(4-ヒドロキシナフチル) プロパン等があげられ、特に2, 2-ビス(4-ヒドロキシフェニル) プロパンが好ましい。またこれらのビスフェノール化合物は2種以上の混合物でもよく、更に他の2価の化合物、例えば2, 2'-ジヒドロキシジフェニル、ジヒドロキシナフタレン、ヒドロキノ、レゾルシノール、2, 6-ジヒドロキシクロベンゼン、2, 6-ジヒドロキシトルエン、3, 6-ジヒドロキシトルエンなどの混合物を用いてもよい。

【0017】芳香族ジカルボン酸としてはテレフタル酸、イソフタル酸、又はこれらの混合物が好ましい。またこれらのテレフタル酸及びイソフタル酸はハロゲン又は炭素数1~8のアルキル基で置換されていてもよい。更にこれらに加えて少量の他の芳香族又は脂肪族ジカルボン酸あるいはその機能誘導体を共重合してもよい。

【0018】本発明に使用されるポリエステルエラストマーは、一般に芳香族ジカルボン酸成分(1)、炭素数3以上の低分子量グリコール成分(2)及びポリオキシアルキレングリコール成分(3)から構成されるが、耐

熱性の面から70mol%以上が1種のジカルボン酸成分で構成されることが好ましい。

【0019】前記(1)成分としては、テレフタル酸、イソフタル酸、2, 6-ナフタレンジカルボン酸、2, 7-ナフタレンジカルボン酸、1, 5-ナフタレンジカルボン酸、4, 4'-ジフェニルエーテルジカルボン酸、4, 4'-ジフェニルスルホンジカルボン酸、4, 4'-ジフェノキシエタンジカルボン酸等が考えられるが、特に好ましくは、テレフタル酸及び2, 6-ナフタレンジカルボン酸が挙げられる。かかるジカルボン酸は1種のみを用いても2種以上を併用してもよい。

【0020】前記(2)成分としては、テトラメチレングリコール、ヘキサメチレングリコール等の炭素数3以上の脂肪族グリコールが好ましく用いられるが、ビスヒドロキシエトキシビスフェノールA又は4, 4'-ビスヒドロキシエトキシジフェニルスルホン等の芳香族基を有するグリコールやシクロヘキサジメタノール等の脂環族基を有するグリコールも用いられる。

【0021】前記(3)成分としてはポリオキシプロピレングリコール、ポリ-1, 2-ブチレンエーテルグリコール、ポリオキシテトラメチレングリコール、ポリオキシペンタメチレングリコール、ポリオキシヘキサメチレングリコール、ポリオキシヘプタメチレングリコール、ポリオキシオクタメチレングリコール、ポリオキシノナメチレングリコール等が考えられる。これらの中で特に好ましくは、ポリオキシテトラメチレングリコールである。これらのポリオキシアルキレングリコールは共重合されたものはもちろんランダム及びブロック共重合されたものも用いることができる。

【0022】本発明に用いる(B)、ポリアリレート又はポリエステルエラストマーの合計量は1~20重量部であり、好ましくは5~15重量部である。そして、この(B)成分は優れた熱成形性をシートに賦与するのに効果がある。

【0023】本発明に用いる臭素化合物よりなる難燃剤(C)には、臭素化ビスフェノールA型ポリカーボネート、臭素化エポキシ、臭素化ポリスチレン、臭素化イミド、臭素化ジフェニルエーテル等が挙げられる。

【0024】本発明に使用される臭素化エポキシ難燃剤は下記の構造(II)である。

【化2】



*



($m = 2 \sim 3$)

(111)

※ 20



★



40

50

【0033】この(E)には難燃効果を損なわない限り、パーフルオロアルキルビニルエーテルなどのモノマーを少量共重合することも可能である。添加量は0~2 PPHRである。(E)成分を加えることにより、難燃時

に熔融ポリマーが滴下し難くなり、然うして滴下による二次の燃焼が発生し難くなる。

【0034】本発明のポリエステル樹脂組成物には更にその目的に応じ所望の特性を付与するため、その物性を著しく損なわない範囲で、他の添加剤、例えば無機充填剤、着色剤、紫外線吸収剤、離型剤、帯電防止剤等を添加することができる。

【0035】次に本発明のシートを構成する組成物をシート化する方法について述べる。本発明のシートは、一般に用いられる公知の設備と方法、即ち押出機に、本発明を構成する組成物又は／及び成分を供給し、スリット状のダイスを通して押出し、キャストドラム上にて冷却、固化せしめてシート化することによって得られる。

【0036】本発明の組成物及び／又は成分を押出機に供給する方法としては、例えば①各成分を混合した後、押出機により熔融混練押出してペレットを調整し、しかる後該ペレットを用いてシートを作成する方法、②一旦組成の異なるペレットを調整し、そのペレットを所定量混合してシート作成の押出機に供給しシートを得る方法、③シート作成の押出機に各成分の1又は2以上を直接仕込む方法などいずれの方法も用いることができる。また、この他に、一旦作成シート及び／又は熱成形品及び／又は熱成形した際に発生する抜き屑を粉碎してフレーク化したもの①～③のシート化の際の材料又は成分の1として使用することもできる。また成分の一部を細かい粉体としてこれ以外の成分を混合し添加することは、これら成分の均一配合を行う上で好ましい。なお、ペレットや成分を押出機に供給するに先立って乾燥しておくのが好ましい。

【0037】ペレットを乾燥する方法としては、例えば100℃以上でポリエステルの融点より30℃低い温度の範囲内の温度、より好ましくは120℃以上でポリエステルの融点より50℃低い温度の範囲内の温度に加熱した空気又は窒素ガス等を、必要に応じ除湿して用いて乾燥する方法や電磁波を用いて乾燥する方法等が適用される。

【0038】またキャストドラムの際に、フィルム又はシートに静電気を負荷させ、冷却ドラムに密着せしめるようにすると平面性の優れたフィルム又はシートを得ることができる。

【0039】上述の如くして得られた本発明のシートは熱成形を施さずそのまま裁断等して用いてもよいが、該シートを熱成形することによってさらに多様な用途に役立てることができる。

【0040】上記の如くして得られたフィルム又はシートは、赤外線ヒーター、熱板ヒーターあるいは熱風等によって予熱されたのち、熱成形に供される。

【0041】熱成形の方法としては、メス型、あるいはメス型とオス型もしくはプラグを用い、例えば真空成

形、圧空成形あるいは真空圧空成形が採用される。成形に際して、メス型、オス型及びプラグは加熱することができる。

【0042】

【用途】本発明によって得られた難燃性シート及びこのシートよりなる熱成形品は、例えば電気、電子機器の部品、OA機器の部品、電動工具など機械部品あるいはモーター等の絶縁材料、カードの基材、建築材料等に有益に使用されるが、特にその用途が限定されるものではない。

【0043】

【実施例及び比較例】以下、実施例及び比較例によって本発明を詳述する。本発明に関するシートの難燃性及び成形性は、次の如くして評価した。

【0044】燃焼性：アンダーライターズ・ラボラトリーズのサブジェクト94 (UL-94) の方法に準じ、5本の試験片を用いて燃焼性を試験し、UL-94に準拠してその燃焼グレードを評価した。

【0045】熱成形性：浅野研究所製FC-1APAW型真空圧空成形機に、トレイ状金型を装着して成形し、成形状態を観察することによって評価した。

【0046】表1に記載した組成にて熔融混練した樹脂組成物燃なるペレットを作成し、さらに該ペレットを130℃にて5時間乾燥した後、熔融押出してシート化した。シート厚みは0.3mmであった。

【0047】次いで該シートについて、その燃焼性と熱成形性を評価し、表2に結果をまとめた。

【0048】なお、本実施例及び比較例に用いた各成分は以下のようなものである。

(A) ポリエチレンテレフタレート (PET)

(B) ポリアリレート (PAr)

ポリエステルエラストマー (Ela)

(C) 臭素化ポリスチレン (Br化PSt)

臭素化ビスフェノールA型

ポリカーボネート (Br化PC)

臭素化エポキシ (Br化Epx)

(D) 三酸化アンチモン (Sb・O)

アンチモン酸ナトリウム (Sb・Na)

(E) 微粉状ポリテトラフルオロエチレン (PPTFE)

【0049】

【表1】

	組成					特性	
	(A)	(B)	(C)	(D)	(E)	熱成形性	機械性
実施例	1 PET: 82	PAR: 7	Br化PSt: 8	Sb・O : 3	-	良	V-2
	2 PET: 68	Ela: 9	Br化PC : 17	Sb・O : 7	-	良	V-0
	3 PET: 59	PAR: 5	Br化PC : 22	Sb・Na: 8	-	良	V-0
	4 PET: 79	Ela: 8	Br化Epx: 13	-	-	良	V-2
	5 PET: 91	PAR: 6	Br化Epx: 10	Sb・O : 3	P-PTFE: 0.07	良	V-2
比較例	1 PET: 100	-	-	-	-	良	HB
	2 PET: 90	PAR: 7	Br化PSt: 8	Sb・O : 1	-	良	HB
	3 PET: 47	Ela: 10	Br化PC : 28	Sb・O : 15	P-PTFE: 2.5	不良	V-0

欄右側の数字は(A), (B), (C), (D):重量部、(E):PHRである。

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